A new perspective on metals and other contaminants in fluoridation chemicals*

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Background: Fluoride additives contain metal contaminants that must be diluted to meet drinking water regulations. However, each raw additive batch supplied to water facilities does not come labeled with concentrations per contaminant. This omission distorts exposure profiles and the risks associated with accidents and routine use.
Objectives: This study provides an independent determination of the metal content of raw fluoride products.
Methods: Metal concentrations were analyzed in three hydrofluorosilicic acid (HFS) and four sodium fluoride (NaF) samples using inductively coupled plasma-atomic emission spectrometry. Arsenic levels were confirmed using graphite furnace atomic absorption analysis.
Results: Results show that metal content varies with batch, and all HFS samples contained arsenic (4.9–56.0 ppm) or arsenic in addition to lead (10.3 ppm). Two NaF samples contained barium (13.3–18.0 ppm) instead. All HFS (212–415 ppm) and NaF (3312–3630 ppm) additives contained a surprising amount of aluminum.
Conclusions: Such contaminant content creates a regulatory blind spot that jeopardizes any safe use of fluoride additives.

Keywords: Fluoride additives, Metal contaminants, Drinking water regulations

Background

Prior studies have linked human ingestion of heavy metals to agricultural applications of municipal wastes and commercial fertilizers.[1–3] However, fluoride additives used in the water fluoridation process are another potential source for metal ingestion by humans and have not yet been adequately investigated. The production of fluoride additive involves phosphate rock, which contains cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), mercury (Hg), nickel (Ni), vanadium (V), uranium (U), and other radionuclides and metals at levels that vary by geographical origin.[2–4] Metal contaminants in fluoride additives are a potential contamination source of the water supply.

In an attempt to limit hazardous exposures via drinking water, the US Environmental Protection Agency (EPA) requires that quality and safety assurance programs screen the metal content of drinking water after the use of additives like fluorosilicic acid (H_2SiF_6 or hydrofluorosilicic acid [HFS]), sodium fluorosilicate (Na_2SiF_6), and sodium

fluoride (NaF). The EPA recommends that finished drinking water have fluoride at the desired levels of ≤1.2 mg/l (less than one-third the EPA Maximum Contaminant Level, MCL), while other contaminants stay at or below levels considered safe (<one-tenth the respective EPA MCL).[5,6] Silicate has no MCL, but there is a 16 mg/l maximum drinking water level (MDWL) restriction, and radionuclide levels are not to exceed detection limits of EPA Test Method 900.0.[5–7]

Both the American Water Works Association (AWWA) and the National Sanitation Foundation International (NSF) provide guidelines for the selection and use of fluoride additives. Quality controls consist of multiple standards (i.e., ANSI/NSF Standards 60 and 61, ANSI/AWWA B701-B703) and testing and certification programs.[5,6,8] When an NSF certified additive is dosed into water according to the specified maximum use level (MUL) (typically 6.0 mg/l for HFS; 2.3 mg/l for NaF; 2.0 mg/l for Na_2SiF_6), the dilution process should limit the doses of metals delivered to the public via fluoridation. However, data from 2000 to 2006 and 2007 to 2011 show that controlled dilution procedures resulted in detectable levels of up to 13 metal contaminants and that in finished drinking water samples 43–50% had detectable As; <1–2% had Pb; 0–1% had Cd; and

<1% had Cr.[5,6] Controlled dilution is intended to restrict contaminants to concentrations at or below the ANSI/NSF Standard 60 single product allowable concentration (SPAC) limits (0.1 MCL for contaminants except fluoride) and thereby lessen concern for metal exposure originating from fluoridation.

The controlled dilution process does not protect public safety in the case of accidents and therefore it is necessary to shift focus from regulation of diluted fluoride products to raw fluoride additives – which are never contaminant free. In the United States, state and local agencies are responsible for regulating the use of raw fluoride additives and on numerous occasions these authorities have had to deal with mishandling accidents.[9–22] Such accidents fall into one of three categories: water distribution overfeeds (fluoride levels ≥ 4 or ≥ 7 mg/l in school systems); non-overfeeds (fluoride levels >1.2 mg/l but <4 or <7 mg/l in school systems); and industrial accidents during the handling, transport, or storage of additives at or near water treatment facilities. Regardless of category, fluoride is typically the only contaminant identified or monitored during accidents. Overfeed accidents occur when the MUL is exceeded and excess fluoride additive enters the drinking water. This can result in illnesses in children and adults, attributed to fluoride and not to fluoride combined with other contaminants such as As and Pb.[23–26] In non-overfeed accidents, the public may not be informed for up to 12 months that their drinking water has fluoride levels>1.2 mg/l as long as the MCL of 4 mg/l is not exceeded. Furthermore, the public is never informed about the concentration levels of the other contaminants also present in the water.

In an industrial accident in Utah where a water facility storage tank ruptured and released 300 gallons of HFS, authorities anticipated the high levels of fluoride (495 ppm) in the nearby waterway, but did not anticipate the coexisting 42.6 ppb arsenic discovered during the follow-up investigation. The manufacturer's material safety data sheet (MSDS) on file for the spilled HFS did not warn of any potential arsenic content.[27] This example demonstrates how gaps in regulation allow unreported metal content to become potential health risks during accidental exposure to raw or improperly diluted fluoride additives.

Contaminant content defines exposure and determines health impact. It is well established that batch-to-batch variation in contaminant content can change biological response and that even trace amounts of contaminants can lower the threshold dose for an effect, particularly when there are synergistic interactions and the overall effect is greater than the sum of effects caused by contaminants acting alone.[28]

Synergism between contaminants fosters an underestimation of risks, like that occurring with combinations of Pb, As, Cd, and Cr or fluoride coexisting with aluminum or beryllium.[29–35] Combinations of contaminants can also trigger chemical degradation, generating decomposition products with toxicity greater than that of the original compounds. In a previous trace contaminant study of commercially available HFS samples, one in four samples had signs of decomposition where an unexpectedly high level of hydrofluoric acid (3.3%) exceeded the AWWA standard (1%).[36]

The MSDS's for fluoride additives do not specify threshold limit values for decomposition products such as hydrogen fluoride. While they do warn against combining fluoride with metals to avoid corrosion, they do not describe the risks that decomposition creates for workers as a result of airborne contamination. Although the MSDS's for HFS and NaF additives list a threshold limit value (TLV) of 2.5 mg(F)/m^3, they avoid the 0.5 ppm TLV (0.41 mg(F)/m^3 at 25°C and 760 Torr) for occupational exposure to hydrogen fluoride.[37] This incomplete disclosure can result in unexpected outcomes, like that encountered by manufacturers of fluoroether compounds (i.e. sevoflurane) when trace amounts of metal oxides from metallic or glass surfaces of containers or medical devices initiated chemical degradation to form highly toxic levels of hydrogen fluoride, hydrofluoric acid, and silicon tetrafluoride.[38–41] Any metal initiated degradation of fluorinated compounds is important to consider, especially since drinking water increasingly contains fluorinated pharmaceuticals.[42,43] Beryllium oxyfluoride, barium fluoride, or magnesium fluoride are acutely more toxic than compounds such as sodium fluoride, calcium fluoride, or magnesium oxide.[44–46] Given established hierarchies in potential toxicity, it is important to consider the risks associated with the combination of metals and fluoride in an exposure scenario.

To understand the risks associated with using fluoride additives, it is necessary to first evaluate the metal content of the raw fluoride product before the application of controlled dilution procedures. While NSF programs require annual unannounced inspections of fluoride additive suppliers, inspection results are kept private by nondisclosure agreements to protect business interests. There is no routine screening for discrepancies between inspection results and the manufacturer's Certificate of Analysis or MSDS sent with each additive batch.[5,6] Description of the metal content of raw additives is typically limited to total percent levels (i.e., heavy metals such as lead, <0.0200%) and not the actual concentration of metal per batch. Furthermore, many of the additives imported to the US have errors in their Certificates

of Analyses.[27] Regardless, there are currently no routine measures of metal content per additive batch before use. Currently, fluoride additive purchases are based on AWWA and NSF Standard 60 certification, availability, and cost, but not on metal contaminant content. As of 2013, only one New Hampshire water facility had a low arsenic requirement for fluoride additives (personal communication, D. Paris, Manchester Water Treatment Plant). Utah recently passed legislation (HB 72) requiring the full disclosure of metal contaminant levels in raw fluoride additives.[47]

The aim of this study was to analyze the metal content of NSF certified raw fluoride additives. Unlike previous studies of additive chemical composition, the analyses presented in this study are independent of chemical supplier data, address both liquid (HFS) and solid (NaF) forms of fluoride additives, and focus on multiple metals, not just arsenic.[36,48] This paper also expands on safety considerations in the event of an accident, arguing that NSF's dilution approach, which focuses on one contaminant at a time, is inadequate. Such data are crucial as water facilities that fluoridate are adding potentially harmful contaminants, some carcinogenic, to drinking water.

Methods
Fluoride additives
All the fluoride additives analyzed in this study were commercially available products intended for fluoridation use at US water facilities.

Three HFS additives (HFS-1, HFS-2, and HFS-3) from different batch shipments were selected for study. Each sample was a clear liquid and consisted of 23–25% acid. The HFS additives originated from the US or Mexico (Juarez) and were labeled as AWWA/NSF certified. The origin of individual samples could not be established because manufacturer shipments were stored in common bulk tanks not cleaned between batches. The HFS samples selected for laboratory study were shipped and stored in polyethylene containers prior to analysis.

Four samples of solid fluoride additives were obtained for laboratory testing. One NaF sample (NaF-1) was in white powder form, while the remaining samples (NaF-2, NaF-3, and NaF-4) were in granular form. Each sample was taken from a different batch shipment and all samples selected for laboratory analysis were shipped and stored in individual Teflon containers. All NaF samples originated from Shanghai, China and met AWWA and NSF Standard requirements. Cross-contamination between domestic and foreign made dry additives was unlikely because US production ceased years ago. In contrast, cross-contamination between shipments of different fluoride compounds, some

intended for purposes other than fluoridation, could not be ruled out. Cross-contamination between fluoride salts originating from different countries could also not be ruled out. US suppliers repackage foreign made fluoride salts using the same equipment regardless of source and there is no wet cleaning between uses.

Analytical procedures
All fluoride additive samples required dilution in order to be within the analytical range of the testing instruments. Concentration levels of aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silver, thallium, vanadium, and zinc were determined using EPA's Method 200.7 for inductively coupled plasma-atomic emission spectrometry (ICP).[7] Percentage levels of fluoride and sodium were determined for all additive samples and the percentage of silicon dioxide was determined in the NaF samples and in the samples of HFS-1 and -2. The ICP determined arsenic results were confirmed by reassessment of levels using Graphite Furnace Atomic Absorption (GFAA) analysis.

Report values
Concentration values (micrograms per milliliter for liquid additives and micrograms per gram for solid additives) were expressed as parts per million (ppm) and reported when they equaled or exceeded the method detection limit (MDL) established per analyte. All concentration levels presented in the results, including those for MDL determinations, were from the raw (undiluted) fluoride additive. Each concentration value reported was an average of duplicate measures for intra-laboratory verification.

Results
Some of the results from the chemical analysis were consistent with the content expected of an AWWA and NSF certified fluoride additive. The 23–25% HFS samples contained 18–19% fluoride and sodium content of the four NaF samples met expectations (56%, NaF-1; 56.8%, NaF-2; 54.9%, NaF-3; and 57.4%, NaF-4). The sodium content of the HFS additives was 0.11% (HFS-1), 0.14% (HFS-2), and 0.05% (HFS-3). Based on two measurements, the SiO_2 content of the HFS samples ranged from 16.15% (HFS-2) to 16.55% (HFS-1). The SiO_2 content of the NaF samples was higher than expected: 24.6% in NaF-1, 26.6% in NaF-2, 26.0% in NaF-3, and 25.7% in NaF-4.

Of the 21 metal contaminants analyzed, 12 had concentration levels that were below established MDL's in the raw HFS and NaF additive samples. The contaminants with insignificant concentrations

Table 1 Contaminants with concentration levels below MDL's in raw 23–25% hydrofluorosilicic acid (HFS-1, -2, and -3) and sodium fluoride (NaF-1, -2, -3, and -4) additive samples

Analyte	MDL* (ppm)
Antimony	10.0
Beryllium	1.5
Cadmium	2.0
Chromium	10.0
Copper	10.0
Manganese	20.0
Molybdenum	10.0
Nickel	15.0
Selenium	25.0
Silver	10.0
Thallium	20.0
Vanadium	10.0

*Method detection limit

and the established MDL's per contaminant are provided in Table 1.

The remaining contaminants, including aluminum, arsenic, barium, calcium, iron, lead, magnesium, potassium, and zinc, had concentration levels that exceeded MDL's in at least one of the fluoride additive samples tested. The contaminant concentrations for the liquid HFS samples are presented in Table 2. Contaminant concentrations for the dry salt NaF additives are listed in Table 3.

Arsenic, lead, and zinc were found only in HFS additives. Arsenic in particular was present most consistently. The GFAA analysis confirmed reportable levels of arsenic in the three HFS additive samples (4.9, 34.0, and 56.0 ppm, Table 2). The HFS sample with the lowest arsenic level also contained a reportable level of lead (10.28 ppm, HFS-3, Table 2).

Barium was the only metal contaminant found exclusively in NaF additive samples (13.3 ppm, NaF-1 and 18.0 ppm, NaF-3; Table 3). Reportable levels of aluminum, calcium, iron, magnesium, and potassium were found in both the liquid and dry salt fluoride additives and concentration levels were similar in HFS and NaF samples. Concentration levels of potassium and aluminum were higher in the dry salt additives; with aluminum concentrations in the NaF samples nearly 10-fold higher than those in HFS samples. In general, aluminum was the contaminant with the highest concentration levels.

Discussion

This study demonstrates that the metal contaminant content of raw fluoride additives is highly batch-dependent. There was as much as a 10-fold difference between batches in the concentration levels of arsenic, lead, and barium, contaminants classified as a risk to human health by the National Primary

Table 2 Metal contaminant concentrations found using ICP analysis of raw 23–25% hydrofluosilicic acid additives (HFS-1, -2, and -3). Values are not corrected for density of 1.2 g/ml

Analyte	MDL* (ppm)	HFS-1 (ppm)	HFS-2 (ppm)	HFS-3 (ppm)
Aluminum	10.0	415.0	385.0	212.2
Arsenic	15.0	38.1	20.6	<15.0
	2.0[†]	56.0[†]	34.0[†]	4.9[†]
Barium	5.0	<5.0	<5.0	<5.0
Calcium	25.0	84.5	89.3	90.9
Iron	5.0	714.0	173.0	27.6
Lead	10.0	<10.0	<10.0	10.3
Magnesium	25.0	30.9	31.6	32.2
Potassium	50.0	80.0	68.0	<50.0
Zinc	10.0	27.3	<10.0	<10.0

*Method detection limit.
[†]Value determined using GFAA and a dilution of 0.1 ml/100 ml.

Table 3 Metal contaminant concentrations found using ICP analysis of raw sodium fluoride additives (NaF-1, 2, -3, and -4)

Analyte	MDL* (ppm)	NaF-1 (ppm)	NaF-2 (ppm)	NaF-3 (ppm)	NaF-4 (ppm)
Aluminum	10.0	3393.0	3630.0	3397.0	3312.0
Arsenic	15.0	<15.0	<15.0	<15.0	<15.0
	2.0[†]	<2.0[†]	<2.0[†]	<2.0[†]	<2.0[†]
Barium	5.0	13.3	<5.0	18.0	<5.0
Calcium	25.0	87.6	69.6	67.8	64.8
Iron	5.0	94.3	60.9	82.6	58.7
Lead	10.0	<10.0	<10.0	<10.0	<10.0
Magnesium	25.0	41.4	49.4	40.8	43.6
Potassium	50.0	192.0	221.0	346.0	171.0
Zinc	10.0	<10.0	<10.0	<10.0	<10.0

*Method detection limit.
[†]Value determined using GFAA and a dilution of 1 g/100 ml.

Drinking Water Regulations.[49,50] As no two additive samples were found to have the same exposure profile in this study, assumptions about metal content are unreliable if based on manufacturer source or certification by NSF. Although the AWWA affirms the HFS purchasers' right to know the source of a raw product when manufactured outside North America,[8] such information is meaningless when there is cross-contamination between HFS shipments stored in common tanks. Likewise, cross-contamination may impact metal content when all imported salt additives, regardless of source, chemical form, or intended usage are handled in the same repackaging equipment. The fact that NaF samples in this study were obtained from bulk supplies not yet repackaged, suggests that the unexpectedly high SiO_2 levels were more a function of mislabeling than cross-contamination. Contrary to label and lot number information, this analysis revealed that salt samples were likely an unidentified mix of NaF and Na_2SiF_6, two frequently used fluoride additives with different MUL's and chemical properties. Whether mislabeling or cross-contamination, the findings here indicate that users of fluoride additives can expect unpredictable amounts of metal contamination.

The only consistencies observed among the additives was that certain contaminants were always absent (e.g., antimony, silver, and vanadium), while others were always present (e.g., aluminum, magnesium, and iron). The absent contaminants are consistent with those absent in EPA test samples of tap, pond, and well water.[7] When compared to the content reported for other substances (Table 4), contaminant concentration levels of raw HFS additives were typically much higher than those found in tap water or in industrial or sewage treatment primary effluents.[5–7,51] Moreover, contaminant concentration levels in raw NaF additives were much lower than those reported for contaminated solids with two notable exceptions. Barium and aluminum levels approached those that the EPA found in samples of electroplating sludge, river sediment, and hazardous soils (Table 4). The high and unpredictable contaminant levels found in the samples indicate the upper limits of possible exposures during fluoridation accidents when dilution's mitigating influence is inaccurate or altogether absent. Thus, the results here indicate that NSF's dilution approach is inappropriate. Employees who handle fluoride additives require a fail-safe strategy that takes into account the variable and hazardous metal content of the additives, both for their safety and the safety of consumers.

Arsenic has been reported as the "limiting constituent" for HFS dosage when controlling contaminants

Table 4 Measured contaminant levels in raw fluoride additives compared with measurements in environmental test samples

Analyte	Concentration levels (ppm) in raw fluoride additives*	Concentration levels (ppm) in aqueous and solid matrices reported in the literature
Arsenic		
HFS	4.9–56.0	0.0006 or 0.00166 average in tap water fluoridated by NSF certified HFS[†]; <0.02 in industrial effluent[‡]
Lead		
HFS	<10.0–10.3	0.0006 or 0.0011 average in tap water fluoridated by NSF certified HFS[†]; 0.251 in industrial effluent[‡]; 0.015 in sewage treatment primary effluent[‡]
Barium		
NaF	<5.0–18.0	39.8 in electroplating sludge[§]; 54.8 in river sediment[§]; 111 in hazardous soil[§]
Aluminum		
HFS	212.2–415.0	0.185 in tap water[‡]; 1.19 in sewage treatment primary effluent[‡]
NaF	3312–3630	4980–5160 in electroplating sludge, hazardous soil, and river sediment[§]
Calcium		
HFS	84.5–90.9	35.2 in tap water[‡]; 500 in industrial effluents[‡]
NaF	64.8–87.6	28 000–85 200 in river sediment, electroplating sludge, and hazardous soil[§]
Magnesium		
HFS	30.9–32.2	8.08 in tap water[‡]; 6.84 in industrial effluent[‡]; 22.7 in sewage treatment primary effluent[‡]
NaF	40.8–49.4	1950–24 400 in electroplating sludge, river sediment, and hazardous soil[§]
Iron		
HFS	27.6–714.0	0.008 in tap water[‡]; 1.28 in sewage treatment primary effluent[‡]
NaF	58.74–94.3	16 500–84 800 in river sediment, electroplating sludge, and hazardous soil[§]

*Data from Tables 2 and 3 of this study.
[†]Data from NSF's Tables 1 and 2.[5,6,51]
[‡]Data from EPA's Table 6.[7]
[§]Data from EPA's Table 7.[7]

in finished drinking water.[36] The range of arsenic levels found in raw HFS samples was 4.9–56 ppm, similar to previous research analyzing raw HFS additives (9.4–58.5[52] and 28–60 ppm[48]). Dilution reduces the parts per million arsenic levels of raw HFS additives, to parts per billion (μg/l) arsenic levels in finished drinking water, allowing concentrations to meet established enforceable drinking water regulations. The current NSF/ANSI standard for arsenic is 0.001 ppm (1 ppb based on an MCL of 0.010 ppm).[5,6,49,50] Table 5 provides the arsenic levels expected in finished drinking water when HFS is used for fluoridation. For example, Weng *et al.* calculated that 60 ppm arsenic in raw HFS additives would contribute 0.245 μg/l arsenic in finished drinking water fluoridated at 1 ppm (Table 5).[48] Using this calculation, the 56.0 ppm arsenic found here in one HFS sample would become 0.224 μg/l arsenic in finished drinking water when fluoridated at 1 ppm. As long as dilution is controlled and fluoridation stays at 1 ppm, arsenic levels (0.019–0.245 ppb in Table 5) in finished drinking water stay below the 1 ppb Standard 60 level. However, during fluoride overfeeds only the HFS additives with the lowest arsenic levels (4.9 μg/l in Table 5) can produce drinking water where arsenic meets the Standard 60 level of 1 ppb. Moreover, fluoride non-overfeeds risk exceeding the Standard 60 level of 1 ppb arsenic when HFS additives contain high levels of arsenic (56.0–60 μg/l). The risk is even greater when there are multiple sources (e.g., natural erosion or non-fluoride water treatment chemicals) contributing arsenic to finished drinking water. Water treatment chemicals other than fluoride additives can contribute up to 0.061 μg arsenic/l of finished drinking water.[48] Combine this 0.061 μg/l arsenic with the 0.956 or 0.873 μg/l arsenic contributed by fluoride additives (raw additives containing 56 or 60 ppm arsenic; Table 5), and the total either exceeds the 1 ppb standard or comes close enough that there is no allowance for input from natural sources. Fluoride, but

not arsenic, is typically monitored daily when treated water enters the water delivery system. In contrast, arsenic levels are only checked quarterly or annually, depending on individual facility protocols. While HFS related non-overfeeds mean that fluoride levels are below the 4 ppm MCL/MCLG standard, it does not necessarily mean that arsenic is below the 1 ppb standard, or that arsenic is even the highest concentration contaminant of concern. The low arsenic HFS additive identified in this study (4.9 ppm arsenic) also contained 10.3 ppm lead (current NSF/ANSI standard=0.0015 ppm; MCL=0.015 ppm). The NaF additives contained neither arsenic nor lead, but did contain up to 18.0 ppm barium (current NSF/ANSI standard=0.2 ppm; MCL=2 ppm).[5,6,49,50] Therefore, the use of arsenic as the "limiting constituent" may not be appropriate.

The arsenic, lead, and barium content of raw fluoride additives pit health risks against technological feasibility and drinking water regulations. For these contaminants, standards are based on health concerns, technology, and cost.[49,50] Technological allowances are for geogenic sources that contribute substantially to source water contamination. In short, standards are relaxed to allow for arsenic, lead, and barium to be introduced into drinking water via erosion of natural deposits.[49,50] When present in fluoride additives, these contaminants are added to natural sources of contaminants, complicating control over site-specific erosion problems and in turn the estimation of total contaminant exposure. Without such allowances, the standards would be solely health-based and provide margins of safety adequate to protect against adverse health effects. Such health-based standards are the EPA's Maximum Contaminant Level Goals (MCLG's), which are set at 0 ppm for arsenic and lead, and 2 ppm for barium.[49,50] The 0 ppm MCLG for arsenic was established because arsenic exposure is associated with skin and cardiovascular damage, lung cancer,

Table 5 Raw HFS additive arsenic content converted to concentration levels expected in finished drinking water with fluoridation at desired (1 ppm), non-overfeed (3.9 ppm), and overfeed (24–200 ppm) dilutions

Raw HFS additives – analytical results for arsenic (ppm)	Finished drinking water – calculated estimate* of arsenic concentrations (μg/l) during desired, non-overfeed, and overfeed fluoride situations		
	Desired F-level 1.0 ppm	Non-overfeed F-level 3.9 ppm‡	Overfeed F-level 24 ppm§
56.0†	0.224	0.873	5.38
34.0†	0.136	0.530	3.26
4.9†	0.019	0.076	0.470
60‖	0.245¶	0.956	5.88
28‖	0.114¶	0.446	2.75

*Calculation method of Weng *et al.*[48]
†HFS solution designated as 24.0%.
‡Fluoride non-overfeed range=1.2–4.0 mg/l.
§Reported accidental fluoride overfeed level.[13]
‖Reported HFS analytical result for arsenic[48] (24.5% HFS solution).
¶Reported finished drinking water arsenic level.[48]

and bladder cancer. Similarly, the 0 ppm MCLG was established for lead because lead exposure can cause physical and mental developmental delays, attention and learning deficit disorders, kidney damage and hypertension. The 2 ppm MCLG for barium was created because of its hypertensive effects. The MCLG of zero indicates that any amount of lead or arsenic in drinking water, whether derived from natural or artificial sources, poses a risk to human health.

While it is known that arsenic in HFS increases the numbers of lung and bladder cancers in the United States,[53] no consideration has been given to the arsenic and lead levels in HFS overfeeds and non-overfeeds. Non-overfeeds are a particularly insidious exposure since they are unreported for months and total contaminant contribution is ignored. As water operators continue to focus only on desired fluoride levels (1 ppm), health consequences will be systematically underestimated and potential carcinogens may enter into the public water system.

The high levels of aluminum in raw fluoride additives raise questions about the adequacy of current drinking water regulations. Along with calcium, iron, and magnesium, aluminum is regulated under the National Secondary Drinking Water Regulations as a technical and a esthetic nuisance, not as a risk to human health.[49,50] Some nuisance contaminants are considered essential and possibly protective against cardiovascular and cerebrovascular mortality.[54,55] In drinking water, aluminum and iron can cause undesirable color, tastes, and/or odors, but neither has an enforceable MCL for health-based concerns. Federal regulations do not require state health agencies and public water systems to monitor aluminum levels in water supplies, and aluminum levels are not determined when an NSF certified fluoride additive is dosed into water at a MUL.[5,6,49,50] Aluminum is not a limiting constituent for any water treatment chemical and is only restricted when an aluminum-based flocculant is used to remove naturally occurring excess fluoride and/or unwanted color and turbidity from water supplies.[36,56,57] After this removal process, residual aluminum levels should not exceed 0.2 ppm. This concentrations is low enough that drinking water contributes a much smaller proportion of the lifetime burden of aluminum than food.[49,50,58,59] However, this flocculation limit does not relate to the later process of fluoridation, which is the last step in water treatment before drinking water is delivered. It is assumed that NaF additives contain only small amounts of aluminum.[60] This is not a safe assumption given the 212–415 ppm aluminum found in the HFS samples and the near electroplating sludge levels (3312–3630 ppm) found in the NaF samples (Table 4). Findings from this study indicate that

fluoride additives deliver a larger proportion of the daily aluminum intake than previously realized, and unknown concentrations of aluminum fluoride complexes are reaching consumers via fluoridation.

Concerns that aluminum in drinking water threatens health are countered by claims of low toxic potential due to poor gastrointestinal (GI) absorption.[61] The level of alumino-hydroxide complexes in city water supplies (21.8 ± 10 µg/l[58]) seems trivial compared to the 400 mg of aluminum hydroxide found in one over the counter antacid tablet. However, this comparison is misleading. Although only a small portion of the antacid aluminum gets absorbed, it is enough to accumulate and cause premature osteoporosis, encephalopathy, and proximal myopathy during renal insufficiency.[62] Manufacturers of antacids counterbalance aluminum with magnesium hydroxide in order to cancel the adverse effects the two metals have on the bowel.[62] Furthermore, patients are warned not to take antacids concomitantly with certain medications because aluminum hinders essential drug absorption by forming Al-drug insoluble complexes.[62] This exceptional binding strength is why aluminum is no longer used as a phosphate binder to treat renal osteodystrophy. It promotes adynamic bone disease (low bone turnover), anemia, myopathy, and dementia.[63] In short, aluminum exposure via antacids is not comparable to exposure from drinking water. Antacids contain aluminum in the hydroxide form. Aluminum in food additives is usually in the form of a sulfate, silicate, or phosphate,[64] and human absorption of aluminum sulfates and silicates is largely unknown, while that of relatively insoluble aluminum phosphates depends upon the amounts consumed.[65] Gastrointestinal absorption of aluminum varies by quantity and chemical form.[66,67] Drinking water contains multiple forms of aluminum, including aluminum–fluoride complexes, which are readily absorbed in the GI tract and cross the blood–brain barrier.[32,68,69] It is the aluminum–fluoride complex form that has the greatest potential for biological impact, where toxicity stems from mimicking gamma-phosphate, altering enzyme activity and activating guanine nucleotide-binding proteins (G-proteins), which are integral to endocrine and nervous system functions.[60,70–78] Al–fluoride complexes have been shown to be markedly more toxic than fluoride alone regarding deposition of aluminum in the brain and kidney and cerebrovascular and neuronal integrity.[32] The much greater biological impact of the Al–fluoride complex, or fluoride coexisting with aluminum or beryllium, constitutes a threat to human health no longer dismissible on the basis of poor GI absorption.

Contaminant interactions should be considered in determining drinking water regulations. The finding of high aluminum levels in raw fluoride samples

underscores the inadequacy of regulations based on SPAC limits. There is no justification for the disparate limits, 0.2 ppm for aluminum and 1.2 ppm for fluoride, especially when the greatest toxic concern is the Al–fluoride complex. To build in a margin of safety, other contaminants have limits that are one-tenth their MCL. In contrast, the 1.2 ppm fluoride limit is less than one-third its MCL, providing no margin of safety to cover the potential toxicity of Al–fluoride complexes. While prior studies have investigated the potential link between Alzheimer's disease and aluminum in drinking water at levels as low as 0.1–0.2 ppm,[79–82] it may be more important to investigate the association between Alzheimer's and levels of Al–fluoride complexes.

While many variables influence Al–fluoride complex formation, control over the formation starts with the disclosure of aluminum content in raw fluoride additives. When aluminum is only regulated as a water quality nuisance, only fluoride is considered for its potential health effects. Too narrow a focus on fluoride artificially limits populations at risk to those with compromised fluoride excretion (renal insufficiency), excluding those with higher than normal aluminum absorption (e.g., the elderly, Alzheimer and Down's syndrome patients[83,84]). This shortsighted exclusion is avoidable if drinking water regulations addressed exposures to Al–fluoride complexes in addition to individual aluminum or fluoride levels.

In summary, raw fluoride additives contain significant levels of arsenic, lead, barium, and aluminum not addressed by current regulations with health-based standards. These raw product levels establish the upper limits of exposure in the event of fluoride overfeeds, non-overfeeds, and industrial accidents. Although the findings of this study are limited by small numbers of samples and manufacturing sources, they highlight flaws in the quality control of NSF certification. Controlled dilution procedures needed to meet NSF/ANSI standards camouflage the fact that metal contaminants are being removed from water sources only to be returned to finished water supplies via fluoridation. The use of fluoride additives assures that some risk is passed to the consumer, especially with regard to arsenic, lead, and non-overfeed levels of fluoride (1.2–4 ppm) that can persist undisclosed up to a year. Since January 2011, there has been a proposed recommendation to lower the optimum fluoridation level to 0.7 ppm. This proposal remains without regulatory standing and has been ignored. Considering this study's findings, the following recommendations outline controls needed to fill the gaps in current regulations:

1. All metal contaminants with concentrations that reach or exceed MDL's of analytical instrumentation should be identified per batch shipment, regardless of source, before being used as a treatment chemical in public water supplies. Records of actual contaminant concentrations should be kept and made available to the public on request and to first responders during accidental spills.

2. Fluoridation levels should not exceed 0.4 ppm (one-tenth the fluoride MCL) in order to provide a margin of safety for interacting contaminants. Fluoridation above 0.4 ppm should not be attempted unless the aluminum and beryllium in raw additives are at levels below MDL's.

3. Raw additives with low arsenic, lead, and barium levels should be used when source waters contain these contaminants in naturally high concentrations. If such additives are unobtainable, the use of fluoride additives should be discontinued.

4. In conjunction with the use of fluoride additives, aluminum should have an established MCL and be regulated under the National Primary Drinking Water Regulations.

There must be a concerted effort to improve transparency with respect to the contaminant content of raw fluoride additives. Adopting the above recommendations would be a major step in alleviating the growing concerns for safety.

Disclaimer statements

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